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I have funding to support one student through the AASERT program. Over the past three years, I have split this money between four students, Todd J. Martinez, Lawrence E. Carter, Claudine C. Tazartes, and Michelle R. Radeke. I now briefly describe their research accomplishments related to the AASERT grant. (All of them have more than satisfactory grades and all are U.S. citizens.)

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AASERT Final Technical Report

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June 30, 1995

I have funding to support one student through the AASERT program. Over the past three years, I have split this money between four students, Todd J. Martinez, Lawrence E. Carter, Claudine C. Tazartes, and Michelle R. Radeke. I now briefly describe their research accomplishments related to the AASERT grant. (All of them have more than satisfactory grades and all are U. S. citizens.)

Todd Martinez was the primary student supported on this grant, and he earned his Ph. D. in September 1994. His thesis involved utilizing pseudospectral numerical approaches to the electron correlation problem, with the goal of developing accurate methods that scale better than current analytical methods such that larger molecules can be treated with configuration interaction (CI) or perturbation theory. In the past three years, we have published four papers and one book chapter due to appear this summer (reprints/preprints of which were sent to AFOSR already) on this subject. The first concerned the development of pseudospectral full configuration interaction [*Journal of Chemical Physics*, **97**, 1876 (1992)], the second discussed the creation of pseudospectral double excitation configuration interaction [*Journal of Chemical Physics*, **98**, 7081 (1993)], the third presented pseudospectral many-body perturbation theory through third order [*Journal of Chemical Physics*, **100**, 3631 (1994)], the fourth formulated pseudospectral multireference single and double excitation configuration interaction [*Journal of Chemical Physics*, **102**, 7564 (1995)], and the book chapter is a pedagogical review of pseudospectral electron correlation methods emphasizing its relationship to other approaches (to appear in "Modern Electronic Structure Theory," edited by D. R. Yarkony, in the World Scientific Advanced Series in Physical Chemistry). We have shown that while pseudospectral full CI can be accurate but not practical under today's data storage conditions, truncated CI and perturbation theory calculations in fact show a distinct advantage in scaling while retaining chemical accuracy. For example, we have demonstrated that our pseudospectral MP2 code is an order of magnitude faster than existing commercial codes (Gaussian 92) for moderate-sized molecules with modest basis sets, and is expected to be even faster for molecules with extensive basis sets. Our pseudospectral MP3 code is extremely accurate and also faster than Gaussian 92, with expected speedups of more than an order of magnitude for large molecules. Todd's pseudospectral multireference single and double excitation configuration interaction method for arbitrary spin states turns out to be even more accurate than our MP2 method (average error for a series of molecules is 0.2 kcal/mol in the total energy), and up to six times faster than conventional spectral methods. We are extremely encouraged by the speed and accuracy of these new methods for treating electron correlation that we have developed in the last few years, and expect to continue our development of these methods in the years to come.

Lawrence E. Carter was the second most supported student on this grant. He is finishing up his thesis this summer. He carried out Monte Carlo and ab initio-derived molecular dynamics simulations of SiGe superlattice structures and F_2 and F atom/Si(100) reaction dynamics. Four papers have been published in the last two years, one is about to be submitted for publication, and two more are in preparation (the published papers have been sent to the AFOSR in preprint and reprint form). The SiGe superlattice simulations [*Journal of Vacuum Science and Technology A*, **11**, 2059 (1993)] were designed to ascertain the atomic level structure of Si_xGe_{1-x}/Si and Si_xGe_{1-x}/Ge electronic devices. In addition, we developed a split-box pseudo-constant pressure technique used in this work to allow fast equilibration of two solids in contact with one another. We were interested in comparing the structures near the interface between the SiGe alloy and the pure

elements (Si or Ge) to see if either the composition or the lattice size varied from what would be expected for the bulk alloy. Indeed, certain types of superlattices do exhibit changes in composition and lattice size. For Si_xGe_{1-x} grown on silicon with high Ge content in the alloy, we saw an increase of Ge atom concentration near the interface, which we argued was favored thermodynamically in order to reduce strain in the alloy layers. In addition, all the superlattices exhibit a significant complementary expansion or compression of the alloy lattice perpendicular to the interface as a means of relieving the parallel interfacial strain. The F_2 reactive scattering on Si(100) was the first study in a series to ascertain the kinetics of surface processes, including etching of silicon. We calculated reaction probabilities for F_2 impinging on clean silicon, as a function of translational and vibrational energy in the F_2 molecules [*Journal of Chemical Physics*, **100**, 2277 (1994)]. We find that translational excitation is slightly more effective than vibrational excitation at increasing the reactivity of F_2, but that vibrational excitation is most effective for producing precursors leading to etching (SiF_2). We find that F-atom abstraction, where one Si-F bond is formed while the other F atom in the F_2 molecule leaves the surface, is a very probable reaction due to the enormous exothermicity of the reaction (>100 kcal/mol exothermic to deposit only one F on the silicon surface and >200 kcal/mol to deposit both F atoms). These scattered F atoms do not have time to equilibrate with the surface, as is illustrated by the fact that they are translationally hot and do not come off in a cosine distribution. We also studied the reaction of F_2 molecules with stepped [*Journal of Vacuum Science and Technology A*, **12**, 2235 (1994)] and defective [*Surface Sci.*, **323**, 39 (1995)] Si(100) surfaces. We find that because the reaction is so exothermic, the reaction is insensitive to the presence of steps or defects, and indeed is merely concerned with the number of dangling bonds (sp^3 hybrid radical electrons) available to form bonds to F. This an extremely useful result from the experimentalist's perspective, because it says that it does not matter how defective your surface is, it should have similar reactivity towards F_2. We have also carried out extensive work on the reactive scattering of F_2 and F atoms on partially fluorinated surfaces and at higher incident translational energies of the F_2 molecules. We have discovered we can tailor the branching ratio between two reaction pathways just by varying the translation energy of the F_2, with atom abstraction dominant at low energies and dissociative chemisorption dominant at high energies [*Journal of the American Chemical Society*, to be submitted, July 1995]. Other interesting dynamical trends are emerging, such as an insensitivity of the kinetic energy of ejected F atoms to the initial energy of the impinging F_2 molecules, that lend themselves to designing a new means of anisotropic etching of Si. We will send preprints as they are submitted this summer, with more details, since I understand this report was to be only a very brief summary of the work.

Two other students have been supported by this grant for a few months each. Claudine Tazartes is a mathematics graduate student who is working on refining the pseudospectral method to improve its accuracy. She is pursuing this by calculating the exact alias (numerical error) for atoms and homonuclear diatomic molecules and projecting that alias onto a set of functions in order to minimize both the error and the size of the set of dealiasing functions required. Michelle Radeke has been writing a kinetic Monte Carlo code that we plan to use to study etching of silicon very soon. She has also been working on calculating transition state theory rate constants from ab initio multireference CI calculations for a number of reaction pathways for hydrogen desorption from silicon, as well as exploring the reaction of NH_3 with the silicon (100) surface. The hydrogen desorption work is nearly finished, and we will be sending a preprint shortly [*Surface Sci.*, to be submitted, July 1995].